ULTRASONIC ATTENUATION STUDIES

IN SUPERCONDUCTING LEAD

by

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ABSTRACT

Measurements of the attenuation of 10, 30, 50 and 70 MHz longitudinal sound waves, propagated in the [100], [110] and [111] directions, have been conducted on the normal and superconducting states of high purity unstrained lead.

Analysis of the data has been presented in such a manner as to allow for the possibility of multiple superconducting energy gaps. Our data indicate the existence of a secondary gap. The data have also been compared to theoretical calculations for both weak and strong coupling models.

Measurements of the ultrasonic attenuation have also been conducted on a sample of strained lead for the [100] direction. Preliminary statements have been made with respect to strain effects and a simple descriptive model has been proposed.

CHAPTER I

INTRODUCTION

Background

The phenomenon of superconductivity was first observed in 1911 by Kamerlingh Onnes¹ who perceived the persistence of a current in mercury which had been cooled below 4.2°K. It was concluded after much investigation that within the limits of the sensitivity of the apparatus the electrical resistance of the material had vanished. By 1913 Onnes had further discovered that the material returned to the normal state if the current exceeded some critical value. This situation persisted until 1916 when Silsbee² hypothesized that the return to the normal state was not due to the size of the current but rather the magnetic field associated with the current. In turn this led to a study of the magnetic properties of superconductors. It was found that the magnetic field necessary to return a superconductor to its normal state was temperature dependent and an empirical description of this was given as³

$$H_c = H_o [1 - (T/T_c)^2], \quad (1)$$

where H_c is the critical magnetic field, H_o is a constant value of field tending to H_c as 0°K is approached, T is the temperature and T_c is the transition temperature to the superconducting state. Further studies of this nature continued on various superconducting materials until

1933 at which time Meissner and Ochsenfeld⁴ found that a superconductor immersed in a magnetic field actually exhibits near perfect diamagnetism so long as the critical field is not obtained. This expulsion of the magnetic field from the interior of a superconductor has become known as the Meissner Effect. It was not until 1950 that the last piece of empirical information was obtained. Working independently, Maxwell⁵ and Reynolds et al.⁶ used several isotopes of mercury and determined the dependence of the transition temperature with respect to the isotopic mass, M . The results have become known as the Isotope Effect and are expressed as⁷

$$T_c \sqrt{M} = \text{constant}. \quad (2)$$

In addition to the empirical evidence there have been many theoretical attempts to explain the phenomenon of superconductivity. Among these have been electrodynamic theories as put forth by F. and H. London⁸ resulting in the London penetration depth which indicates to what extent a magnetic field penetrates a superconductor. Thermodynamic approaches have also been studied such as those by Gorter and Casimir⁹ and more recently by Mühlischlegel¹⁰ which account for such things as the discontinuity in the specific heat at the transition temperature. Physical models were also proposed, the most useful being the two-fluid model of Gorter and Casimir.¹¹ This model consists of envisioning two interpenetrating fluids. One is composed of normal electrons while the other consists of superconducting electrons which appear below the transition temperature. The super-

conducting electrons experience no resistance to flow and hence short circuit the normal electrons which accounts for the disappearance of electrical resistance. It was further assumed that a certain amount of latent heat was necessary to convert normal electrons into superconducting electrons hence the discontinuity in the specific heat.

One of the most comprehensive theories and the one with which we are most directly involved is that of Bardeen, Cooper and Schrieffer¹² (the BCS Theory). This theory derives its meaning through the Isotope Effect and the two-fluid model. The first indicates the possibility of acoustic phonon interactions due to $T_c \approx \sqrt{M}^{-1} \approx \omega$ and final formulation of the theory places the two-fluid model on a firm theoretical foundation. The term phonon is used to describe quantized lattice vibrations. Quantum mechanics tells us the energy of a linear harmonic oscillator is $\hbar\omega$ and this is the quantum of energy associated with the phonon. A given lattice will have many normal modes of vibration and thermal energy will cause phonons with varying frequencies to be present. In addition to the average oscillations in the lattice with respect to temperature, the lattice can be subjected to forced oscillation. Mechanical vibrations may be introduced into the lattice creating phonons of prescribed energies, determined by the driving frequency. These phonons, of course, are subject to collisions with lattice defects, other phonons, electrons, lattice boundaries, etc.

In the early 1950's work had begun on acoustic investigations of superconductors. It was noted that ultrasonic waves propagated in normal metals suffered increased attenuation as the temperature

was decreased and that upon reaching the superconducting state the attenuation decreased rapidly though continuously. Based on these observations, Pippard,¹³ who previously had worked on the London theories, proposed a theory based on interaction between conduction electrons and phonons using the free-electron model of a metal. He viewed the electrons in the metal as a degenerate Fermi gas enclosed in a box which was subjected to periodic distortion. In the absence of collisions the Fermi surface, which in the free-electron model is spherical, would be distorted due to energy absorbed from the acoustic wave. Collisions with the lattice would tend to restore the spherical nature of the surface but as the temperature is lowered the electronic relaxation time would become long enough to allow the Fermi surface to remain distorted, hence absorb the acoustic energy and not re-emit it coherently. In other words as the temperature is lowered the mean free path of the electrons becomes long enough to allow their interaction with the applied phonons. This would thus appear as an increase in the attenuation. His theory provided an analytical determination of the attenuation and yielded a frequency dependence as well. Defining $q = 2\pi/\lambda$ as the magnitude of the wave vector and ℓ as the electron mean free path, in the limit where $q\ell \gtrsim 1$, it was found that the attenuation becomes directly proportional to the applied acoustic frequency. We shall recall this frequency dependence later in our study. Pippard¹⁴ has since refined his work but the basic results involving the propagation of longitudinal ultrasound have remained unchanged.

Soon after Pippard's work the BCS Theory was formulated. This

theory revolved around the assumption of virtual phonon exchange between conduction electrons creating an attractive force between pairs of electrons. The problem of virtual phonon exchange was first considered by Cooper¹⁵ with regard to only two electrons and the problem was then generalized to include many pairs of electrons. A brief description of the BCS Theory as it pertains to this dissertation is given in the Appendix. The exchange of a virtual phonon involves the motion of an electron through the lattice and the ensuing interactions. As a conduction electron proceeds through the lattice it causes distortion due to the coulomb attraction between the positive ions at the lattice sites and the conduction electron. This in turn causes a displacement of neighboring ions and a mechanical vibration has thus been created. This vibration will be transmitted through the lattice and at the proper moment it is possible that another ion, perhaps even several hundred lattice sites away, will create a pull on a second conduction electron in such a way as to cause it to move toward the electron which originally created the disturbance. The net result would appear to be an attraction between the two electrons. Surrounding these electrons, and even between them, other electrons could experience similar interactions. The BCS Theory is based on these interactions and coherence arising between them. We thus have two systems, one involving the conduction electrons and the other being pairs of electrons acting in a coherent fashion. This begins to parallel the two-fluid model quite strongly even to the point of involving a latent heat or energy required to form the pairs. Indeed the BCS Theory offers very good explanations

for the phenomenological observations including such effects as loss of electrical resistivity, the Meissner Effect, London penetration depth, discontinuous specific heat, the Isotope Effect and the problem with which we are deeply concerned, the attenuation of ultrasound. The BCS Theory requires the existence of an energy gap between the superconducting pairs and the Fermi level of the normal conduction electrons. This energy gap will appear at the transition temperature and will increase to a value determined by reaching 0°K. The value of the gap at 0°K is given in the form¹⁶

$$2\Delta(0) = 3.5kT_c, \quad (3)$$

where k is the Boltzmann constant and $2\Delta(0)$ is the zero temperature energy gap. As the temperature decreases below the transition temperature the number of electrons remaining in the unpaired state decreases while the Cooper pairs increase. The frequencies of the applied phonons are kept well below those which would enable interaction with the Cooper pairs. Therefore, the phonons do not have sufficient energies for interaction with the Cooper pairs and the change in attenuation depends only on the normal conduction electrons. This means that with fewer electrons available to interact with an ultrasonic wave passing through the lattice the attenuation decreases with decreasing temperature. The ratio between the attenuation in the superconducting state and the normal state is given by¹²

$$\alpha_s / \alpha_n = 2[1 + \exp.\Delta(T)/kT]^{-1}, \quad (4)$$

where the attenuations are denoted by α_s and α_n signifying superconducting and normal states respectively and $\Delta(T)$ is the temperature dependent energy gap tending toward $\Delta(0)$ at 0°K .

Purpose

Ultrasonic studies dealing with single crystal lead have been carried forth with very little organization. As with most new areas this is understandable due to the eagerness of the individual investigators to observe and report. The result has lead to a saturation of studies involving pure unstrained lead oriented in the [100] direction. Some investigations were extended to include impurity doping, again primarily concerned with the [100] direction. This has created a void with respect to complete directional studies and no real attention has been paid to the effect of strain condition in otherwise pure samples.

In the analysis of data, previous work has generally assumed a single energy gap parameter. The data were curve-fit to Equation 4 and $\Delta(T)$ was extrapolated to 0°K to compare with the value given by Equation 3. In most cases the analysis has consisted merely of plotting the data against the BCS Theory and determining $\Delta(0)$. A more complete study should incorporate the remaining crystallographic directions and should allow for the existence of any variations from the BCS Theory. Included in this would be a study of the variation of the zero temperature energy gap with respect to applied frequency. Indications should also be given as to the importance which strain dislocations lend to the basic theory and analysis.

This dissertation is concerned with a systematic study of the attenuation of longitudinal ultrasound propagated in the three basic crystallographic orientations of pure single-crystal lead. Longitudinal ultrasonic waves have been propagated in the [100], [110] and [111] directions and attenuation ratios have been noted as a function of temperature. The frequency dependence has also been considered by using 10, 30, 50 and 70 MHz ultrasound in each of the three directions. Although the BCS Theory only accounts for one energy gap, it has been hypothesized¹⁷⁻¹⁹ that the presence of more than one energy gap may exist. Our studies and method of analysis allow for the possibility of more than one energy gap. Evidence has already been presented²⁰ which indicates a multiple energy gap in superconducting mercury. Both lead and mercury tend to depart from the BCS Theory more than other superconductors studied thus far.^{16,21} Thus it would seem reasonable to consider a second energy gap in lead due to the existence of a similar event measured in mercury. Beyond this we felt that the comparison of our data to other existing theories might prove useful. The BCS Theory assumes a weak interaction between electrons and neither lead nor mercury really exhibits this behavior due to the more complex nature of their Fermi surfaces. One of the theories which depends on strong-coupling interactions was put forth by Woo.^{22,23} We have displayed our data beside this theory as well as the BCS Theory in an attempt to further our understanding. Our investigations have included both strained and unstrained samples for the [100] direction in the hopes of discerning a difference based on the dislocations in the samples.^{24,25} The strained crystal was pre-

pared in another laboratory. The crystal was treated in a manner similar to our technique and then strained after the unstrained condition had been reported.²⁶

CHAPTER II

EXPERIMENTAL

Apparatus

The ultrasonic attenuation of superconducting lead was investigated by the single-ended pulse-echo technique.

The electronic equipment, shown in Figure 1, consisted of an Arenberg, 93 ohm, matched impedance network. An R. F. electrical pulse of the desired frequency, and approximately three microseconds duration, was produced by the pulsed oscillator with a repetition of 60 Hz. This pulse travels through a coaxial cable to a coaxial "Tee." Part of the energy travels through the "Tee" to the preamplifier, wide band amplifier and is eventually displayed on the oscilloscope. The remainder of the energy in the pulse is diverted, via the "Tee," to a quartz transducer where the electrical energy is converted into an acoustic wave. The acoustic wave travels through the specimen, reflects from the opposite face and returns to the transducer. The quartz transducer now serves as a receiver, reconverts the acoustic wave pulse into an electrical pulse. This echo pulse travels through the amplifying system and is displayed, together with the initial pulse, on the oscilloscope which has been triggered by the pulsed oscillator. Meanwhile the acoustic wave continues to reflect back and forth in the specimen, losing energy on each successive round trip. Thus, the oscilloscope trace will consist of the initial pulse followed by a train of equally spaced echoes with each successive echo having a smaller amplitude.

Figure 1. Block diagram of experimental electronic equipment.

Figure 2 shows the low temperature cryostat. The cryostat was constructed of brass and stainless steel with a thin-wall stainless steel coaxial transmission line inserted through to the region of liquid helium. Ease of operation was facilitated through the use of numerous "O"-ring seals to allow quick entry and closure of the system. In the upper chamber of the cryostat a vacuum port allowed for evacuation of the interior, monitored by a thermocouple vacuum gauge mounted in the same chamber but perpendicular to the vacuum port axis. Vacuum-tight leads for connections to the thermometry and heater coil were fabricated from bare copper wire inserted through holes in the upper chamber and sealed with Stycast 2850 GT, epoxy-resin.

The transmission line, shown in Figure 3, was constructed from a thin-wall stainless steel tube (1/4 inch) and 26-gauge enameled copper wire. Teflon spacers were used to assure that the wire was coaxial with the tubing. At the top of the line a female BNC connector was soldered to the center wire and then to the outer tubing. The bottom of the line was filled with Stycast 2850 GT. The top was silver-soldered to the upper chamber of the cryostat. This created a vacuum-tight structural seal. The center wire, which extended beyond the epoxy filled end, was wrapped helically to form a spring contact with the sample holder.

Figure 4 depicts the sample holder. It consisted of a base, housing a germanium resistance thermometer and a heating coil, and a spring loaded plunger providing the contact between the transmission line and the transducer resting on the top of the lead sample. The plunger and spring were isolated from the coaxial outer shell by a

Figure 2. Low temperature cryostat.

Figure 3. Transmission line construction.

Figure 4. Detail of the sample holder.

nylon sleeve. This also served as a guide to align the plunger and spring with the sample. The outer shell and base served as the ground side of the system via the metallic sample to establish the electric field across the transducer. The top ring of the sample holder and the base were joined with thin brass rods which were soft-soldered in place. This allowed for repositioning of the base to accommodate samples of varying dimensions with a minimum of effort or re-design. The germanium resistance thermometer, manufactured by Cryocal, Inc., was mounted in a socket in the base immediately below the sample surface and Glyptal was used to insure good thermal contact as well as a semi-permanent installation. The heater coil was wrapped on the lower end of the base and was electrically isolated with successive applications of Stycast 2850 GT. On the bottom of the base, nichrome wire was used to provide three centering arms and also create a slight heat leak to the surrounding helium bath.

The lower portion of the transmission line and the sample holder were then surrounded by a vacuum jacket constructed from thin-wall stainless steel tubing (3/4 inch). This allowed evacuation (5×10^{-3} Torr) during the initial curing and cooling of the sample binder. During an experimental run the interior pressure was raised to 90×10^{-3} Torr by introducing gaseous helium. This served as an exchange gas to cool the sample region.

In operation, the germanium resistance thermometer was adjusted to optimum current conditions as suggested by the manufacturer with the use of a current calibration circuit as pictured in Figure 5. The ranges were 1 - 2°K, 1.0 microamperes; 2 - 15°K, 10 microamperes;

Figure 5. Schematic of Germanium resistance thermometer current standard. (All resistances given in ohms unless otherwise specified.)

15 - 40°K, 0.1 milliamperes. The 2 - 15°K range was used and the current value established using a Leeds and Northrup K-3 potentiometer and a Honeywell null indicator, model 104W1-G. Having calibrated the thermometry, the output of the germanium thermometer was then disconnected from the potentiometer and used to drive the X-Y recorder for the temperature axis.

In actual operation the sample was positioned on the base and the outer jacket was then positioned and the cryostat evacuated. After the lowest pressures had been reached a small Dewar containing liquid nitrogen was placed around the system to begin the cool-down phase. Once this was accomplished the pulse-echo formation was checked on the oscilloscope and a liquid helium transfer was made to the main Dewar system. The entire cryostat was then removed from the liquid nitrogen and inserted into the liquid helium bath. The superconducting data were obtained starting at the lowest temperature and warming the system gradually by slowly varying the current fed to the heater in the base of the sample holder. Then the system was moved between the pole faces of a twelve-inch Varian electromagnet, model V3603 powered by a Varian regulated power supply, model V-FR2501. The magnet was set at one thousand gauss to quench the superconducting state and the normal state data were obtained, again starting at the lowest temperature. The frequency of the signal was then checked on a Hewlett-Packard electronic counter, model 5245L. The frequency was then re-set for the next determination and the sample, having been removed from the magnetic field, was raised above the transition temperature to insure against flux-trapping. The temperature was

again lowered and a new set of data were gathered.

The actual data gathering was accomplished with the aid of a display scanner and an X-Y recorder. The display scanner is an accessory to the Hewlett-Packard, 175A, oscilloscope. It allows a trace on the oscilloscope to be transferred to an X-Y recorder. In our application, the display scanner was positioned at a point on the trace and information regarding the change in the vertical position of that point was relayed to the X-Y recorder. The display scanner was set to monitor the maximum of the first echo. Its output was applied to the Y-axis of the recorder. The germanium resistance thermometer's voltage output was attached to the X-axis. Thus we were able to continuously monitor the change in the echo voltage with respect to the change in temperature, noted in ohms due to the standard current applied to the resistor. Figure 6 is a reproduction of such a recorder plot. A given set of data was obtained over a temperature range of 2 to 12°K. This was done to assure the existence of continuity between the normal state data and data gathered after the superconducting state had been raised above the transition temperature and returned to the normal state. Periodically the voltage as recorded was checked by a Tektronix oscilloscope equipped with a voltage comparator. The calibrated output of the comparator was also used to calibrate the X-Y recorder. The X-Y recorder trace was accurate to ± 0.02 volts based on a signal strength of approximately 6.0 volts and between $\pm 0.01^\circ\text{K}$ in the 2°K region and to $\pm 0.07^\circ\text{K}$ in the 12°K region. The pulse and detection circuitry was found to be stable to 0.5%. The thermometry was accurate to $\pm 0.01^\circ\text{K}$. To assure the

Figure 6. Reproduction of data obtained in both the superconducting and normal state of single-crystal lead for longitudinal sound waves (50 MHz) travelling in the [110] direction.

absence of amplitude dependent effects²⁷⁻²⁹ several runs were made at increasing power levels. During these runs the gain of the amplifiers was kept constant. It was noted that within the power range of our experiment there was no observed amplitude dependence. All of the observations made may thus be explained by other than amplitude effects.

Sample Preparation

The samples were cut from single-crystal lead obtained from Research Crystal, Inc., specified to be 99.9999% pure. They were spark-cut and spark-polished using an electrical discharge machine, model TQH-31 manufactured by Elox. Spark-cutting the surfaces eliminates mechanical shock and thermal transfers associated with standard cutting techniques thereby preserving the integrity of the single-crystal. The surface damage, according to the manufacturer, is restricted to less than one one-thousandth of an inch. The samples were oriented to within one degree of the preferred directions [100], [110] and [111] with Laue back-reflection X-ray photographs. After spark-working and orienting, the samples resembled cubes of approximately five millimeters on a side.

After the final polishing and before the binder application, the surface was cleaned thoroughly. Dilute nitric acid and sodium hydroxide alternately spaced with rinsings of distilled water were used. The binder and quartz transducer were then applied and the sample placed under the plunger contact in the cryostat.

Transducers and Binders

The transducers, obtained from the Valpey-Fisher Corp., were

thin quartz wafers of 1/8 inch diameter. They were cut for a fundamental frequency of 10 MHz and polished for overtone operation utilizing odd harmonics. Both faces of the wafer were plated with gold. This allows for a uniform electric field to be placed across the transducer thereby converting electrical energy into mechanical energy due to the piezoelectric behavior of quartz.

In order to transmit the mechanical wave from the transducer to the crystal it is necessary to have a bond between them. In this study both Nonaq vacuum grease and Dow Corning 250,000 centistokes silicon fluid were used as bonding material. The binder was applied very sparingly to the sample using a needle point to obtain the minuscular portion of binder used. The transducer was then placed on top and slowly rotated to eliminate air pockets and assure even distribution.

CHAPTER III

ANALYSIS OF DATA

After the applied frequency was established and the pulse-echo system and the low temperatures had been obtained, the plots of echo voltage versus temperature were created using the display scanner and X-Y recorder. The height of the first echo, as previously described, was converted to attenuation values in decibels per centimeter. The level of the echo height at the transition temperature was used as a reference point. As an example shown in Figure 7, this gave values of both plus and minus attenuation about the relative zero obtained at the transition temperature. Our interest lies in the attenuation effects due to the conduction electrons hence in the superconducting state at 0°K there should be zero attenuation. The assumption was made that the background attenuation due to binder loss, lattice effects, impurities, etc. was independent of temperature within the range of our investigations and could be subtracted from the gross attenuation. Figure 8 displays the result which left the attenuation referenced to zero at 0°K in the superconducting state. Although the quantities of interest involve the attenuation ratio, α_s/α_n , it was necessary to investigate the effect which crystal dimensions experienced in the superconducting and normal states. The room temperature lengths of the crystals were corrected to our temperature range using the coefficients of thermal expansivity as given by White.³⁰ These values were given for both superconducting and normal

Figure 7. Attenuation values taken from Figure 6, referenced to the transition temperature (T_c), for the [110] direction at 50 MHz.

Figure 8. Attenuation values corrected for temperature independent background for the [110] direction at 50 MHz.

state lead. It was found that while a difference existed it amounted to a variance of one part per ten thousand with respect to changes in length. Thus we ignored the difference and simply used relative attenuations for each sample to determine α_s/α_n . These values were, of course, corrected for the basic temperature change, but no distinction was made between superconducting and normal state lengths.

Once the attenuation ratio was determined, equation 4 was rewritten to give

$$2[\Delta(0)/kT_c]G(t)/t = 2\ln[2\alpha_n/\alpha_s - 1], \quad (5)$$

where $G(t) = \Delta(T)/\Delta(0)$ and $t = T/T_c$. This allows the superconducting energy gap to be determined graphically as the slope of $\ln[2\alpha_n/\alpha_s - 1]$ versus $G(t)/t$. The values for $G(t)/t$ were calculated for an ideal superconductor in accordance with the work of Mühlischlegel.¹⁰ This analysis technique,²⁰ unlike a single parameter curve-fit to the zero temperature energy gap, allows for the existence of more than one zero temperature energy gap. This possibility is not excluded by the BCS approach although not explicit in the original work.¹⁷⁻¹⁹ Any major deviation from a straight-line plot should indicate the presence of more than one gap. Figures 9 through 12 readily indicate, for our data, there is a strong deviation from a straight-line plot. A complete set of zero temperature primary energy gaps, in terms of $2\Delta(0)/kT_c$, is given in Table 1. The secondary gaps cannot be determined with the precision of the primary gaps from our data. However, our determinations of the secondary gaps, $2\Delta(0)/kT_c$, from these

Figure 9. Plot of $\ln[2\alpha_n/\alpha_s - 1]$ versus $G(t)/t$ for listed directions in Pb at 10 MHz.

Figure 10. Plot of $\ln[2\alpha_n/\alpha_s - 1]$ versus $G(t)/t$ for listed directions in Pb at 30 MHz.

Figure 11. Plot of $\ln[2\alpha_n/\alpha_s - 1]$ versus $G(t)/t$ for listed directions of Pb at 50 MHz.

Figure 12. Plot of $\ln[2\alpha_n/\alpha_s - 1]$ versus $G(t)/t$ for listed directions in Pb at 70 MHz.

Table 1. Values of $2\Delta(0)/kT_c$ for listed directions and frequencies in Pb.

Direction of Wave Propagation		Frequencies (MHz)	$2\Delta(0)/kT_c$
[100]	(strained)	10	4.33
		30	4.25
		50	4.47
		70	4.45
[100]	(unstrained)	10	2.54
		30	3.18
		50	3.97
		70	4.38
[110]	(unstrained)	10	2.58
		30	3.33
		50	4.03
		70	4.33
[111]	(unstrained)	10	2.63
		30	3.05
		50	3.98
		70	4.47

plots yield values of 2.14 for the strained [100] crystal and 1.50 for the unstrained [100], [110] and [111] crystals. The strained crystal in both the initial and secondary energy gaps exhibit higher values than do the unstrained crystals.

The unstrained crystals were prepared in our laboratory as previously described. The strained crystal was obtained from Deaton²⁶ and was prepared in a similar manner. The crystal was originally prepared in the unstrained state and then subjected to a small impulsive shock to induce the strain.³¹ The unstrained results previously reported by Deaton²⁶ compare quite well with our results in the [100], [110] and [111] directions as do those of Fate et al.³² for the unstrained [100] direction.

Next we considered the frequency dependence of the zero temperature primary energy gap as shown in Figure 13. We note the existence of a linear frequency dependence for the unstrained crystals and the absence of the effect for the strained crystal. The value of $2\Delta(0)/kT_c$ for the strained case was found to be an average of 4.38.

The final analysis involves a comparison of our data against the calculations of the BCS Theory and the strong-coupling model attributed to Woo.^{22,23} Figures 14 through 17 show the BCS values for α_s/α_n , calculated for $2\Delta(0)/kT_c = 3.5$,³³ versus the temperature ratio, t , and our experimental data for the various frequencies and associated directions. Again we see the definite change with the applied frequency for the unstrained cases and no apparent change for the strained case. As an additional comparison we have used Woo's values for α_s/α_n in the near vicinity of the transition temperature

Figure 13. Plot of $2\Delta(0)/kT_c$ versus the applied frequency in MHz.

Figure 14. Plot of the attenuation ratio, α_s/α_n , versus the temperature ratio, T/T_c , in the [100] direction in strained Pb for listed frequencies.

Figure 15. Plot of the attenuation ratio, α_s/α_n , versus the temperature ratio, T/T_c , in the [100] direction in unstrained Pb for listed frequencies.

Figure 16. Plot of the attenuation ratio, α_s/α_n , versus the temperature ratio, T/T_c , in the [110] direction in unstrained Pb for listed frequencies.

Figure 17. Plot of the attenuation ratio, α_s/α_n , versus the temperature ratio, T/T_c , in the [111] direction in unstrained Pb for listed frequencies.

and our data in this region.³⁴ Perhaps some additional information may be obtained due to lead's deviation from the weak-coupling assumptions as mentioned in the introduction. Figures 18 through 21 yield the results of this comparison. Woo's calculations are given in terms of q values while ours, to be consistent with our text, are given in frequencies. Table 2 relates the applied frequencies to the associated q values at these temperatures in single-crystal lead. These values were calculated from the elastic constants of lead as given by Waldorf and Alers³⁵ in conjunction with density values given in the American Institute of Physics Handbook. The density was corrected for temperature using the coefficients of thermal expansivity as mentioned before.³⁰ As can be seen, the experimental values span values which surround the BCS Theory and proceed toward the predictions of Woo's model.

Figure 18. Comparison of data to the calculations of Woo and the BCS Theory about the transition temperature for the [100] direction in strained Pb.

Figure 19. Comparison of data to the calculations of Woo and the BCS Theory about the transition temperature for the [100] direction in unstrained Pb.

Figure 20. Comparison of data to the calculations of Woo and the BCS Theory about the transition temperature for the [110] direction in unstrained Pb.

Figure 21. Comparison of data to the calculations of Woo and the BCS Theory about the transition temperature for the [111] direction in unstrained Pb.

Table 2. Values of the phonon wave vector and corresponding frequencies between 2 and 12°K.

Frequency (MHz)	Phonon Wave Vector (cm ⁻¹)
10	289
30	866
50	1444
70	2021

CHAPTER IV

CONCLUSION

Observations

The first observation to be noted is the absence of anisotropy of the energy gap for the unstrained crystals. This was to be expected and raises no contradiction with previous work.³⁶ However, the difference between strained and unstrained states was quite apparent. Our results for the strained [100] direction appear to be in mild contradiction to a previous study by Fate et al.³² Their results indicated that the primary energy gap for a strained lead crystal exhibited a small frequency dependence. In earlier studies^{26,28,32} in the [100] direction, on unstrained lead, the primary energy gap was found to exhibit a frequency dependence in accordance with our results for unstrained crystals. Furthermore, this frequency dependence for the unstrained lead was in the reverse order to that found by Fate in the strained crystal. These results would indicate that pure unstrained lead crystals exhibit a definite frequency dependence in the primary energy gap. The frequency dependence is linear and would thus correspond quite well to the theories put forth by Pippard.¹³ It would appear that as the crystal is strained this frequency dependence becomes diminishingly small and eventually it reappears in the reverse order under more severe strains. This subject will be treated more thoroughly in a later section of this chapter.

The second observation is concerned with what appears to be a

second energy gap with the magnitude being roughly half that of the initial gap. The existence of a second gap is not entirely unexpected.¹⁷⁻¹⁹ Studies²⁰ similar to ours, though performed on single-crystal mercury, have revealed secondary energy gaps. Due to the deviations of both lead and mercury from the assumptions of the BCS Theory, as mentioned in the appendix, it is not unreasonable to anticipate a second energy gap in lead after the previous observation of the same event in mercury. It has been theorized³⁷ that multiple energy gaps may arise in materials with more complicated Fermi surfaces. Lead has four valence electrons and as such has a complicated Fermi surface structure⁴² as depicted by Figure 22. The valence electrons of lead lie in the 6s and 6p shells. Matthias et al.³⁷ believe that the band structure of a metal yields a different density of states for the s and p states near the Fermi surface. In effect this means that the band associated with p-electrons has a different superconducting energy gap with respect to the Fermi surface than do the s-electrons. They mention that for very complicated band structures where there are "n" distinct Fermi surfaces that "n" distinct energy gaps should exist.

While our work yields no definite statement other than the existence of the secondary gaps, which heretofore have not been reported, it would appear from our observations and those of Newcomb and Shaw²⁰ that the secondary energy gap could be more precisely studied at higher frequencies (above 0.5 GHz). Higher frequencies appear to reveal the secondary gap at temperatures much closer to the transition temperature. This would allow for more accurate determinations of

First zone

Second zone

Third zone

Fourth zone

Figure 22. Fermi surface in the first four Brillouin zones of pure lead⁴².

attenuation, based on this gap, with respect to temperature. This would allow the secondary gap to be seen at lower values of $G(t)/t$ thereby allowing precise values of the slope to be obtained. Once this is accomplished, in-depth studies may be undertaken with respect to frequency dependence, strain effects, anisotropy, etc.

The last observation is concerned with the comparison of our data to the BCS Theory and strong-coupling model. Our data follows the basic shape as predicted by the BCS Theory. We do, however, see a displacement between our data and the theoretical curve. This displacement might have been anticipated due to lead's preference for a strong-coupling theory. Our curves compared with the strong-coupling calculations of Woo³⁴ lead us to believe, however, that lead is in fact exhibiting behavior which would appear to be similar to the BCS Theory for the lower frequencies used and tending toward the strong-coupling theory as the frequency increases. For the higher frequencies the interactions would appear to be stronger than those proposed in the BCS Theory and yet weaker than that conceived by Woo. We also note that the strained sample may indicate some frequency dependence in the immediate vicinity of the transition temperature. This disappears very rapidly, however, as can be seen in the comparison with the BCS curve over a large temperature range. No significant contribution can be established with regard to this as evidenced in the analysis leading to the primary and secondary zero temperature energy gaps.

Proposed Explanation

The apparent lack of frequency dependence in the zero temperature

energy gap for the strained lead sample in the [100] direction can be explained through the mechanism of dislocation damping. The propagation of sound suffers attenuation due to absorption of acoustic energy by crystal dislocations pinned by impurities. An in-depth theoretical study of the phenomenon has been undertaken by Granato and Lücke²⁴ resulting in the vibrating string model of dislocation damping.³⁸ This model reveals a maximum of attenuation after only a few per cent of plastic deformation has been achieved. In addition the model yields a very good approximation for face-centered cubic metallic crystals of which lead is one example. It has been found that the attenuation maximum varies with both the applied acoustic frequency and the temperature. The maximum attenuation is a resonance phenomenon and according to Tittman and Bömmel³⁹ lies above 150 MHz for pure lead. Not only does the value of attenuation maximum vary with temperature and frequency but the position of the maximum with respect to frequency increases with decreasing temperature. The magnitude of the attenuation increases with increasing frequency and decreasing temperature. The latter dependence is explained by the reduction of thermal phonon drag on the dislocation thereby allowing the dislocation to absorb more acoustic energy and increase its motion.

Tittman and Bömmel have further theorized that α_n is not affected by dislocation damping. They visualize the normal state electrons as a viscous gas which impedes the motion of the dislocations and hence does not appear until the superconducting state is reached. At that point the density of normal state conduction electrons is reduced

and the dislocations are freed to absorb energy. In their studies, which involved amplitude dependence,⁴⁰ an increase in the attenuation, α_s , at a given temperature, was observed due to the increasing dislocation attenuation as a function of decreasing temperature. Although the initial response was that of following the BCS predictions for α_s , as the amplitude was increased, α_s also experienced an increase.

In the determination of the zero temperature gap the only variable affecting the value is the reciprocal attenuation ratio, α_n/α_s . We note that α_n is unaffected by the dislocation damping mechanism but does increase with increasing applied frequency as described by Pippard. The value of α_s is however affected by dislocation damping and the effect appears to be that of decreasing α_s as a function of decreasing temperature. The BCS Theory predicts an exponential decrease in α_s thus the net effect, once the temperature independent background has been subtracted, is to produce a decrease of α_s to a value below the BCS prediction. Figure 23 gives a qualitative account of the combined effects of the dislocation mechanism with respect to the electronic attenuation in the superconducting state. It should be noted that the temperature independent background applies only to the normal state attenuation. Of course this is based on the viscous electron gas as described by Tittman and Bömmel. The superconducting attenuation is affected by both the temperature independent and dependent backgrounds.

The mechanism for the initial decrease in the background and subsequent return to the constant level can also be understood through

Figure 23. Description of the attenuation backgrounds necessary to yield the BCS value for α_s in the case of the [100] direction in strained Pb investigated at 50 MHz.

the interaction of the normal state conduction electrons and the dislocations. Our experiments did not involve amplitude dependence.

In the immediate vicinity of the transition temperature, the interaction between the normal state conduction electrons and the dislocations provides an additional mechanism for the formation of superconducting electron pairs. The dislocations may be viewed as localizing and focusing the exchange of virtual phonons between the conduction electrons. In the perfect lattice, the ordering allows for the randomness of this occurrence. The disordering, due to dislocations, provides a localized point for the exchange of virtual phonons. An analogous situation could perhaps be nuclear boiling in which case imperfections are necessary to create the boiling process. In a perfectly smooth vessel, higher temperatures are required before boiling occurs. Once the number of normal state conduction electrons have been sufficiently reduced, the dislocation is no longer impeded. Energy is then absorbed and the result is a corresponding increase in the background attenuation. We thus observe an initial decrease in the attenuation, to a value below the BCS prediction, and an eventual increase which approaches the BCS prediction.

The result is the appearance of a constant value for α_n/α_s with respect to frequency hence a constant value for the zero temperature energy gap. This would of course also be a function of the density of dislocations. Our data indicate that such a balance has been obtained. It could be further surmised, however, that an increase in the density of dislocations might even produce an apparent decrease in the zero temperature energy gap with increasing frequency. In the

case of the unstrained crystal only a temperature independent background need be considered due to the lack of dislocations. For these crystals we observe a frequency dependence of the zero temperature energy gap which is linear and as mentioned corresponds to Pippard's calculations.

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APPENDIX¹²

Although the BCS Theory gives explanations for loss of resistivity, the Meissner Effect, London penetration depth, discontinuous specific heat and the Isotope Effect, this dissertation is concerned with the problems relating to ultrasonic attenuation. As indicated in Chapter I, equations 3 and 4 are most useful in interpreting the effects of attenuation and for evaluating the zero temperature superconducting energy gap. For a better understanding of these expressions, derivations of each will now be presented.

The initial problem begins by utilizing the free energy of the system (Helmholtz Function)

$$F = W - TS, \quad (A-1)$$

where W is the internal energy of the system, T is absolute temperature and S is the entropy. The system will consist of all the states occupied by the ground pairs, excited pairs and single particles composed of the conduction electrons. The internal energy will be comprised of two components,

$$W = W_{KE} + W_I, \quad (A-2)$$

where W_{KE} is the Bloch contribution or the kinetic energy term and W_I is the interaction Hamiltonian for the Cooper pairs including the coherence effect which accounts for superconductivity. The kinetic

energy term is expressed as

$$W_{KE} = \sum_k |\epsilon_k| [s_k + 2p_k + 2(1 - s_k - 2p_k)h_k], \quad (A-3)$$

where: ϵ_k = Bloch energies measured relative to the Fermi surface
for the momentum state, k ,

h_k = distribution function for the ground pairs,

s_k = probability that either $\vec{k}\uparrow$ is occupied and $-\vec{k}\downarrow$ is unoccupied, or vice versa,

p_k = probability that both $\vec{k}\uparrow$ and $-\vec{k}\downarrow$ are occupied.

The interaction Hamiltonian is given by,

$$W_I = - \sum_{k,k'} V_{kk'} [h_k(1 - h_k)h_{k'}(1 - h_{k'})]^{1/2} [1 - s_k - 2p_k) \\ \times (1 - s_{k'} - 2p_{k'})], \quad (A-4)$$

where $V_{kk'}$ is a positive constant which is a reduced energy term expressing the electron-phonon interaction. The negative sign denotes the attractive nature of the entire term.

We now introduce the distribution function, f , which gives the overall probability of occupancy defined as follows

$$s_k = 2f_k(1 - f_k) \quad (A-5)$$

and

$$p_k = f_k^2. \quad (A-6)$$

We may now consider the free energy in the form,

$$F = 2 \sum_k |\epsilon_k| [f_k + (1 - 2f_k)h_k] - \sum_{k,k'} V_{kk'} [h_k(1 - h_k)h_{k'}(1 - h_{k'})]^{1/2} \times [(1 - 2f_k)(1 - 2f_{k'})] - TS, \quad (A-7)$$

where TS may be expressed in the usual manner,⁴¹

$$-TS = 2kT \sum_{k'} [f_{k'} \ln f_{k'} + (1 - f_{k'}) \ln(1 - f_{k'})]. \quad (A-8)$$

We now minimize the free energy with respect to f_k and evaluate f_k for this condition,

$$2|\epsilon_k|(1 - 2h_k) + 4 \sum_{k'} V_{kk'} [h_k(1 - h_k)h_{k'}(1 - h_{k'})]^{1/2} (1 - 2f_{k'}) + 2kT \ln[f_k/(1 - f_k)] = 0. \quad (A-9)$$

In the initial formulation of the BCS Theory, prior to the formalized interaction Hamiltonian, it was shown that the following relations were valid,

$$h_k = 1/2(1 - \epsilon_k/E_k), \quad (A-10)$$

$$[h_k(1 - h_k)]^{1/2} = 1/2(\Delta/E_k) \quad (A-11)$$

and

$$\Delta = V \sum_{k'} [h_{k'}(1 - h_{k'})]^{1/2} (1 - 2f_{k'}), \quad (A-12)$$

where Δ is the superconducting energy gap and $E_k = +(\epsilon_k^2 + \Delta^2)^{1/2}$. Simultaneously it was assumed that $V_{kk'}$ could be replaced by a constant average matrix element, V , defined for $|\epsilon_k| < \hbar\omega$ and by zero outside this region. Using these relations, equation A-9 reduces to

$$\beta[\epsilon_k^2/E_k + \Delta^2/E_k] = \beta E_k = -\ln f_k/(1 - f_k), \quad (A-13)$$

where $\beta = 1/kT$. Solving this equation for f_k we have

$$f_k = 1/(e^{\beta E_k} + 1). \quad (A-14)$$

This will be immediately recognized as the Fermi-Dirac distribution function. When $\epsilon_k \rightarrow 0^+$, then $E_k \rightarrow \Delta$ for the electrons above the Fermi surface and when $\epsilon_k \rightarrow 0^-$, then $E_k \rightarrow -\Delta$ for the electrons below. Thus the new density of states has an energy gap of 2Δ centered about the Fermi surface.

We will now make immediate use of the function f_k , which has just been derived, to calculate equation 4. The ultrasonic attenuation in the superconducting state is given by

$$\alpha_s \propto \int (1 - \Delta^2/EE') [f(1 - f') - f'(1 - f)] \rho(E) \rho(E') dE, \quad (A-15)$$

where $E = -(\epsilon^2 + \Delta^2)^{1/2}$ (the negative sign is taken to correspond with Δ below the Fermi surface) and:

$$\rho(E) = \text{density of states in energy} = N(0)E/(E^2 - \Delta^2)^{1/2},$$

$N(0)$ = density of Bloch states of one spin per unit energy at the Fermi surface,

$$E' = E + \hbar\nu,$$

ν = applied acoustic frequency,

f = probability that $\vec{k}$ and some spin state is occupied,

f' = probability that $\vec{k}'$ and a different spin state is occupied,

$\therefore f(1 - f') = \text{probability that } \vec{k}(\text{spin}) \text{ is occupied and } \vec{k}'(\text{spin})'$
is unoccupied.

This expression may be rewritten and in the limit for $\hbar\nu \ll kT$ we have

$$\alpha_s \propto 2N(0)^2 \int_{\Delta}^{\infty} (f - f') dE \approx 2N(0)^2 \hbar\nu f(\Delta), \quad (A-16)$$

where the factor of 2 arises from adding the contributions above and below the Fermi surface. For the normal state we have $\Delta = 0$ which leads, under the same assumptions, to

$$\alpha_n \propto 2N(0)^2 \int_0^{\infty} (f - f') dE = 2N(0)^2 \hbar\nu f(0). \quad (A-17)$$

Upon combining α_s and α_n we arrive at

$$\alpha_s/\alpha_n = f(\Delta)/f(0) = 2f(\Delta) = 2/(e^{\beta\Delta} + 1), \quad \text{Q.E.D.} \quad (\text{A-18})$$

We now turn our attention to a development of equation 3. Starting with equation A-12 and incorporating the associated definitions plus the density of states, $N(0)$, we arrive at an expression, in integral form, given as

$$1/N(0)V = \int_0^{\hbar\omega} \frac{d\epsilon}{(\epsilon^2 + \Delta^2)^{1/2}} \tanh 1/2 (\epsilon^2 + \Delta^2)^{1/2}. \quad (\text{A-19})$$

For $T = T_c$, $\Delta = 0$, we reduce this equation to

$$1/N(0)V = \int_0^{\hbar\omega} \frac{d\epsilon}{\epsilon} \tanh(1/2\beta_c \epsilon). \quad (\text{A-20})$$

Under the approximation $kT_c \ll \hbar\omega$, where ω is the Debye characteristic frequency, we may obtain a graphical solution¹⁶ which yields

$$kT_c = 1.14\hbar\omega e^{-1/N(0)V}. \quad (\text{A-21})$$

Previously, from a ground state calculation, it was found that

$$\Delta(0) = \hbar\omega/\sinh(1/N(0)V) \approx 2\hbar\omega e^{-1/N(0)V}, \quad (\text{A-22})$$

where the assumption was made that $N(0)V \ll 1$. Combining A-21 and A-22 leads to

$$2\Delta(0)/kT_c = 3.5, \quad \text{Q.E.D.}, \quad (\text{A-23})$$

where $\Delta(0)$ is the zero temperature superconducting energy gap.

We may also note the reasons for anticipating lead to deviate from a true BCS behavior. If we recognize that $T_c \ll \frac{\hbar}{k}\omega = \theta$, where θ is the Debye temperature, we note that for lead, $T_c = 7.22^\circ\text{K}$ and $\theta = 90^\circ\text{K}$, we do not indeed have as good an approximation as demanded to obtain A-21. We may reasonably expect to see some deviation here as well as in mercury²⁰ where $T_c = 4.2^\circ\text{K}$, $\theta = 70^\circ\text{K}$.